

A NEW PERSPECTIVE ON THE NATURE OF "ORGANIC" SULFUR IN COAL.

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INTRODUCTION

It is generally assumed that the sulfur in coal is distributed among organic sulfur, sulfatic sulfur, and pyritic sulfur compounds (1). ASTM D-2492 which lists the forms of sulfur in coal also assumes that three forms are present--sulfatic, pyritic, and organic sulfur. The organic sulfur value of coal is derived as the difference between the total sulfur content of coal and the amount of pyritic plus sulfatic sulfur i.e., any form of sulfur that is not pyritic or sulfatic sulfur would be counted as organic sulfur. The organic sulfur is generally perceived to occur in covalently bonded C-S compounds like thiophenes, thioethers, and bithioethers (disulfides) (2,3). Elemental Sulfur, which would be accounted for as "organic sulfur", has been mentioned, only in a few references in the literature. Yurovskii (4) in his monumental treatise on 'Sulfur in Coals' provides evidence for the presence of elemental sulfur in coals. Richard, Vick and Junk (5) and White and Lee (6) confirmed the presence of elemental sulfur for several bituminous American coals. In a more recent article, Lee et al (7) report the detection, in a Bevier seam coal, of 3,6-dimethylbenzo(b)thiophene that can be potentially formed by reaction of elemental sulfur with terpenes (Figure 1). Further light on this question was provided by De Roo and Horton (8,9) when they demonstrated that elemental sulfur reacts with simple alkyl aromatics, under mild conditions, to give thiophenic compounds. De Roo (8) showed that such reactions can occur under geochemical settings and conclude that the generation of organic S compounds in petroleum followed this route. Thus, the reaction of elemental sulfur with coal aromatics could, in part, account for the formation of organosulfur compounds found in coal (Figure 2). However, Stock et al.(10) report that pristine coal samples (from the Argonne Premium Sample Coal Bank) are free of elemental sulfur. He suggests that sulfur is not a natural constituent of coal, but that on exposure to air, elemental sulfur, which can account for up to 5% of the total amount of sulfur in the sample, is formed.

In this paper we present a new perspective on the nature of organic sulfur in coal and suggest that the organic sulfur fraction in pristine coal contains sulfur in the form of a coal-polysulfide complex (see Figure 3-- an elemental sulfur precursor) which, in some coals, may constitute in excess of 50% of the organic sulfur fraction. Under suitable chemical/biological environments, this sulfur complex would give rise to free elemental sulfur. The sulfur, thus set free could get dispersed through the coal matrix and would be present in the amorphous form. The amorphous form arises when sulfur precipitates from solution as a result of chemical-reactions, especially when it first appears in the colloidal state. This sulfur would be insoluble in organic solvents and would not be detected by X-ray diffraction.

Experimental evidence using solvent extraction studies (under conditions that will allow the extraction of amorphous sulfur form) and geochemical approaches is presented below supporting the concept of this new polysulfide sulfur form in the "organic" sulfur fraction of coal. If this is true, then research and development efforts to remove the so-called organic sulfur components in coal must take into account this factor., especially since the elemental sulfur or the polysulfide sulfur can react with alkyl aromatic structures in coal creating new thiophenic sulfur compounds from which it is very difficult to excise the sulfur.

EXPERIMENTAL

An Illinois No.6 coal (Herrin No. 6 coal from a west central Illinois Underground mine) from the Illinois Basin Coal Sample program (IBCSP, sample No. 1), the corresponding pristine Illinois No. 6 coal from the Argonne Premium Sample Coal Bank and an Indiana bog(reject) coal were selected for extraction studies. Table 1 shows the sulfur analysis for the three coals studied.

TABLE 1
Analysis for Forms of Sulfur in Coals Studied

Coal	Organic %	Pyritic %	Sulfatic %	Total %
IBCSP No.1	3.00	1.20	0.06	4.26
Pristine Coal				
Indiana Bog	3.33	5.20	4.48	13.01

2g of the coal (accurately weighed) were extracted with perchloroethylene solvent at different temperatures and the extract concentrated. The concentrate was diluted to mark in a 25ml volumetric flask and the amount of sulfur determined using GC-MS. The sulfur quantization was carried out using a Finnigan 4000 gas chromatograph/mass spectrometer (San Jose, CA). A 6' x 2 mm i.d. SP2100 on 80/100 Supelcoport chromatographic column was used with a helium flow rate of 35 ml/min. For these analyses, both the column and injector temperatures were held constant at 180°C. The ion source temperature of the mass spectrometer was set at 180°C. The electron energy was set at 70eV and the electron multiplier 1600eV for these analyses. The mass analysis was carried out using multiple ion detection (MID).

In order to quantitate, a standard curve was first obtained using the following series of standards; 0.005% , 0.01% , 0.025% , 0.05% , 0.1% , and 0.5% sulfur. Five microliters of both the standards and samples were injected on-column. The criteria for confirmation of sulfur was two-fold: 1) retention time and 2) relative ratio of the three sulfur ions used in the MID program (m/z 64:192:256; 10:2:1). The standards were run again after the samples to determine the stability/reproducibility of the ion intensities within the mass spectrometer over the total time of the analysis. The peak area of the m/z 64 ion was used in the quantitation.

RESULTS

COAL SAMPLE STUDIES

Perchloroethylene extraction of Illinois Coal

Perchloroethylene is an excellent solvent for solubilizing elemental sulfur. The solubility is ~ 30g S/ 100g Solution as opposed to only 0.066g S/ 100g Solution in Ethyl Alcohol or 2.7g S/ 100g Solution in Acetone. The Illinois Basin Sample Coal Program sample No.1 (-100 mesh) (IBSCP sample 1) was extracted with perchloroethylene at 120°C and the results of three different runs gave an average elemental sulfur content of 1.54% for the coal sample Table 2).

TABLE 2
Elemental Sulfur in Illinois Coals

Coal/Run No.	% Elemental S	Average %	Elemental S as % of Organic S	Elemental S as % of Total S
IBCSP-1	1.50			
IBCSP-2	1.62	1.54	51.3	36.1
IBCSP-3	1.50			

This means that 51.3% of the so called "organic" sulfur or 36.1% of the total sulfur is present as elemental sulfur. Stock et. al. (10) report that only 2% of the total sulfur in the same type of coal (IBSCP sample 1) was elemental sulfur. However extraction of a pristine Illinois No.6 coal from the Argonne

Sample Coal Bank gave no elemental sulfur within the detection limits used. An Indiana Bog (Reject) coal was extracted with perchloroethylene at different temperatures and as shown in Table 3 there was a 59% increase in the amount of elemental sulfur extracted in going from room temperature to 120°C. The 1.23% elemental sulfur extracted at 120°C amounts to 36.9% of the "organic sulfur" in that coal.

TABLE 3
Effect of Temperature on Sulfur Extraction

<u>Temperature</u>	<u>% Elemental S extracted</u>
Room Temp.	0.78
60°C	1.08
120°C	1.23

Geochemical Approaches

Fresh coal samples from the Minnehaha Mine, Sullivan County, Indiana was used in the study. The method of sampling which was described by Parratt and Kullerud (11) assures that unoxidized specimens are obtained. The samples were divided into approximately equal amounts and placed in ten double polyethylene plastic bags which were sealed airtight and directly transported to storage containers in the Purdue laboratories. One bag was opened within hours upon arrival at the laboratory and its content was exposed its warm, humid air. Oxidation products in the form of a yellowish-brown or other colored powder started to form within days, was quite distinct after one week, and occurred in significant amounts after one month. X-Ray powder diffraction charts made on this substance displayed the characteristic reflections of iron-calcium-aluminum sulfates. The color and texture of this substance are similar to those of elemental sulfur. However, the X-ray powder diffraction reflections of sulfur were not observed. The sulfur, if present, may be amorphous.

A number of polished sections were made on material from a second bag and under the reflected light microscope it was noted that pyrite, marcasite and sphalerite make up about 2% of this coal. Pyrite is most common, marcasite much less so and only one or two grains of sphalerite were observed in each section. Sulfates of any form or elementary sulfur were never observed in freshly made polished sections. Four stages of iron sulfide mineralization are distinguishable; framboidal pyrite, marcasite, fibrous pyrite and massive pyrite. Although these sulfides generally are evenly distributed throughout the coal it was possible to localize areas which contained no visible sulfides. Accordingly, fresh samples from a third bag were gently crushed to about 2 mm size and placed in badges of a few grams at a time under the zoom lense of a binocular microscope. It was now possible to quite efficiently separate grains of coal with no visible sulfides. Several grains of this material were next exposed to warm, humid air. Oxidation products again became visible in a few days. The products were the same, but their amounts were much smaller than those which previously were produced under identical conditions in equal time from the original unseparated coal. About one dozen of the coal grains, containing no visible coal, were mounted in low temperature curing epoxy and polished. Less than 0.05% iron sulfide was observed in the polished surfaces under the reflected light microscope. In such grains sporinite is the most common maceral. Vitrinite, cutinite, and resinite are much less common, and fusinite, sclerotinite are the least common. Microprobe analyses were performed on selected sulfide-free areas of polished surfaces of numerous grains. Analyses revealed that sporinite has a sulfur content of about 2.9 to 3.0%, whereas vitrinite, cutinite and resinite contain from 1.1 to 1.4% S and fusinite, sclerotinite contain about 0.25% S (12).

Simultaneous analysis on iron and sulfur in areas where sulfides are not detected in polished sections always gave Fe values of less than 0.1% Fe. The sulfur concentrations cited above reflect the values remaining upon subtraction of the sulfur required to convert all Fe to FeS₂; in other words, it was assumed that all detected iron is present as disulfide. Thus it becomes apparent, that at least in this particular coal, the concentration of the sulfur which we usually refer to as organic is strongly dependent on the type of maceral in which it occurs. Sulfur is, for instance, almost three times as abundant in sporinite as it is in vitrinite which in turn contains four times as much sulfur as do the typical inertinite macerals.

It is also quite apparent that a significant portion of this maceral sulfur reacts with warm and humid air to produce sulfates and amorphous elemental sulfur. In a series of experiments conducted on the

material contained in a fourth sample bag, total sulfur was, by wet chemical analysis on a representative 5 gr sample, found to be 3.2 ± 0.2 wt%. The sulfide sulfur determined by separating physically and weighing the sulfides from a representative 1 gr sample gave 1.8% sulfide sulfur after correcting, through polished section study, for remaining unseparated sulfides. Wet chemical analysis of the remaining "pure" macerals, which contain less than 0.05% wt Fe and less than 0.2% Al accounted for as clay minerals, gave 1.2 ± 0.2 wt%. Treatment of these "pure" macerals, which had been crushed as cited above, with warm, humid air produced the ocher colored material. This was carefully removed from the maceral grains. New analysis on a portion of the cleaned maceral grains indicated a sulfur concentration of 0.9 wt%. The remaining portion of the cleaned maceral material was finally treated with distilled water for several days at 60°C on a waterbath. Careful processing involving decanting prior to washing in distilled water, repeated decanting and slow drying at 110°C was followed by a final sulfur analysis. This gave 0.6 wt% S. This would indicate that about 50% of the so-called "organic" sulfur can be removed by exposure of the macerals to hot, humid air and to pure warm water. Conservatively stated: at least a portion of the so-called organic sulfur in coal macerals occurs under chemical conditions which permit it to react with oxygen in the air and with water. The character of the chemical bonds involving this particular sulfur is not known, but at least the generally perceived carbon-sulfur bonds are precluded.

DISCUSSION

Both chemical solvent extraction and geochemical studies strongly indicate that the so called "organic" sulfur fraction of coal contains a major sulfur form different from the conventional thiophenic and thioether type structures normally associated with the "organic" sulfur fraction. A coal - polysulfide complex as shown in Figure 3 is suggested. Under suitable chemical/geochemical conditions, this sulfur complex would give rise to free elemental sulfur. This would account for the fact that no elemental sulfur is detected in the Argonne pristine coal sample, however the not so pristine samples from the IBCSP would undergo reaction to yield elemental sulfur. The sulfur, thus set free could get dispersed through the coal matrix and would be present in the amorphous form. Crystalline sulfur (orthorhombic and monoclinic) consist of ring shaped molecules containing eight atoms (Figure 4) and is soluble in common organic solvents like CS_2 and acetone. Amorphous sulfur, on the other hand, results when the ring molecules of sulfur break and successive atoms link together to form a long chain molecule (Figure 4). This would be insoluble in organic solvents and not detected by X-ray diffraction studies. Amorphous sulfur is not stable at temperatures below 160°C and reverts to the crystalline ring-molecule form. This change, however, is extremely slow at room temperatures and at room temperature, amorphous sulfur remains for years with little change (13). At temperatures near 100°C the change from amorphous to crystalline sulfur is more rapid, and practically all amorphous sulfur disappears at this temperature in the course of an hour. The amorphous form arises when sulfur precipitates from solution as a result of a chemical reactions, especially when it first separates as a colloidal dispersed system.. This fits in nicely with the 59 % percent increase in elemental sulfur obtained on going from room temperature to 120°C. It may also be the reason why other investigators using x-ray or solvent extractions at or near room temperatures have not observed appreciable amounts of elemental sulfur. The behavior of the amorphous sulfur is further illustrated in the well known **vulcanization of rubber** using sulfur. In this, a part of the sulfur used for vulcanization remains unreacted, and the vulcanized rubber always contains a certain amount of free sulfur. In the hot vulcanization process, the free elemental sulfur is in crystalline and can be readily extracted with hot acetone or carbon tetrachloride. However, if the vulcanization is effected in the cold, the free sulfur is formed in the metastable amorphous modification and is finely dispersed. It is not extractable even, with good sulfur solvents like CS_2 .

The fact that the coal - polysulfide complex can, under appropriate conditions spit out elemental sulfur is supported by observations on model compounds. Thus, Diethyl Xanthogen trisulfide on treatment with moist acetone forms the disulfide and elemental sulfur while, Diethyl Xanthogen tetrasulfide also yields the disulfide and eliminates two sulfur molecules (14) (Figure 5). One fact that needs to be stressed is that a portion of the sulfur contained in higher polysulfides is so loosely bound that they behave as elemental sulfur and thus, in many reactions behave like elemental sulfur.

IMPLICATIONS

The existence of coal-polysulfide complexes that may yield elemental sulfur and take part in elemental sulfur reactions brings up an important new factor in R&D approaches to removing "organic"

sulfur in coal and for coal processing in general. As shown by White and others (6-9) elemental sulfur can react with alkyl aromatics to form thiophene compounds (Figure 2). Our concern is that coal processing operations result in creation of hard to remove covalent C-S bonded structures like the thiophenes from the more easily removable polysulfide type structures. Even more damaging is the fact that thiophenic crosslinks between coal clusters could arise resulting in the creation of a even more intractable macromolecule (Figure 6) that would be more difficult to process.

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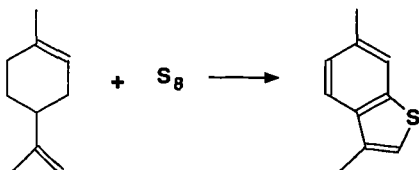


Figure 1. Formation of Thiophenes with Elemental Sulfur. From Ref. 7

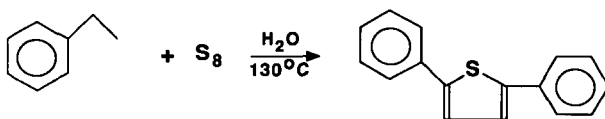
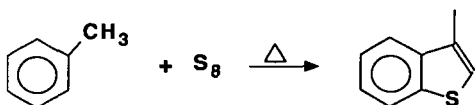


Figure 2. Reaction of Elemental Sulfur with Alkyl Aromatics. Formation of Organosulfur Compounds

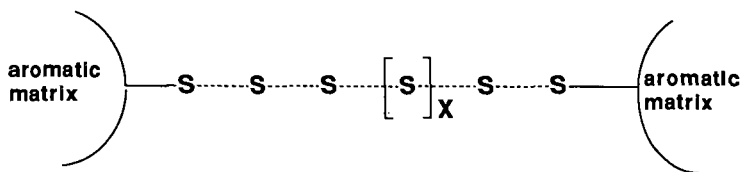
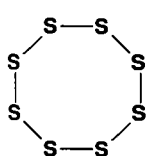
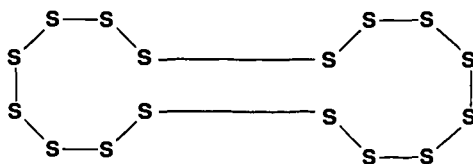


Figure 3. Conceptual Coal-Polysulfide Complex



Crystalline Sulfur



Amorphous Sulfur

Figure 4. Structure of Crystalline and Amorphous Sulfur

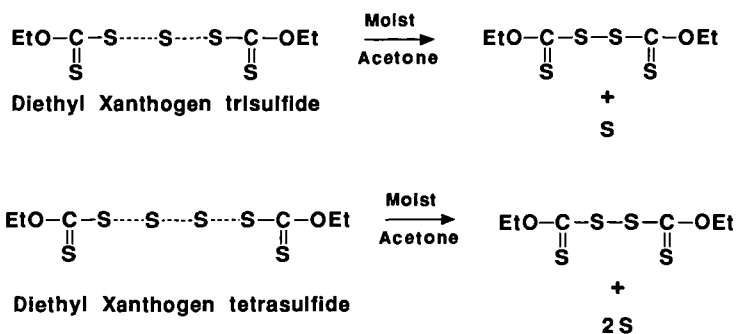


Figure 5. Model Organo-polysulfide Complex Spitting out Elemental Sulfur under Appropriate Conditions

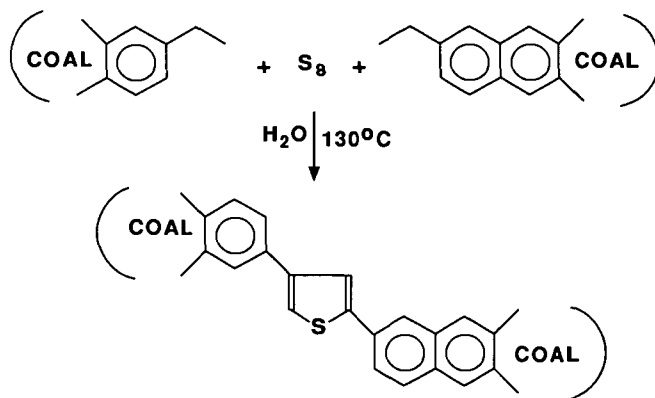


Figure 6. "Crosslinking" of Aromatic Coal Clusters via Thiophenic Bridges